p.211

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(54) **Purifying graphite**

(57) Expanded graphite compounds obtained by treating graphite with sulphuric acid under oxidising conditions, and washing the product with water to replace with water the free sulphuric acid present in it, contain bisulphate ions which are not removed on flash heat expansion (exfoliation) and are responsible for the slight corrosive capacity of material made by compacting the exfoliated stuff. Reduction of such corrosion can be achieved by subjecting the pre-exfoliated water-washed graphite compound to a further treatment with water, in which there is employed water at a temperature above 100°C under superatmospheric pressure or water at a temperature above 30°C with a content of dissolved nitric acid or a nitrate.

GB 2 128 971 A

SPECIFICATION

Method of purifying a graphite compound

This invention relates to a method of purifying a graphite compound.

When natural flake graphite or well ordered synthetic graphite is treated with sulphuric acid under oxidising conditions it swells slightly owing to the interposition, between the layers of hexagonally arranged carbon atoms constituting the graphite lattice, of bisulphate ions HSO_4^- and neutral (unionised) sulphuric acid molecules H_2SO_4. If the slightly swollen material is washed with a large volume of water the intercalated neutral sulphuric acid molecules become replaced by water molecules, but the HSO_4^- ions are largely unaffected. When this compound is freed from adherent wash water and heated for a few seconds at temperatures of the order of 1,000°C, the interstitial water suddenly vapourises and causes a great expansion of the compound in the *c* direction, i.e. perpendicular to the plane of the carbon atom layers, so that the final *c* dimension may be 100 times or even more its initial value. The expanded product, often called 'exfoliated graphite', may (as described in UK Patent Specification 1 049 588) be compacted into flexible material which can be used as gaskets or packing. However, some types of metal become corroded on prolonged contact with flexible material of this kind, and various proposals have been made to reduce the incidence of corrosion by incorporating a corrosion-preventive in the flexible material. Thus US Patent 4 216 266 (= UK 1 596 949) proposes the use as corrosion preventive of an alkali metal salt such as sodium chromate, molybdate or tungstate.

We have approached the problem of corrosion reduction by a different route, and have sought to remove from the graphite compound before exfoliation the bisulphate ions which we regard as prime contributor to the corrosive capacity of compacted forms of the exfoliated products. We believe that free sulphuric acid (which is of course a highly corrosive substance) is generated when the bisulphate compound is exfoliated, and that not all of it escapes during exfoliation. We have tried to remove the bisulphate ions by heating the water-washed graphite compound in water, but even with water at the boiling point this has not been successful.

Our further work, however, has shown that contacting the graphite compound with water at elevated temperature will achieve a useful reduction in bisulphate content, and in the corrosive capacity of compacted forms of the exfoliated product produced from it, provided that it is carried out either at a temperature above 100°C under superatmospheric pressure or in the presence of dissolved nitric acid or a nitrate.

If heating above the normal boiling point of water (autoclaving) is the method adopted, the superatmospheric pressure is conveniently simply that of saturated steam at the operating temperature. Autoclaving is preferably carried out at a temperature of 105-200°C, suitably for 15-120 minutes and at a solids content of 2-20% by weight. Autoclaving may if desired be carried out with a small proportion of an alkaline-reacting agent, preferably a volatile agent such as ammonia, dissolved in the water.

If the bisulphate-removal method chosen is that entailing the use of nitric acid or a dissolve nitrate, the temperature employed should be above 30°C, preferably with a concentration of NO_3^- ions in the range 0.1-2M. Again, the solids content of the system is suitably in the range 2-20% by weight.

Nitric acid or a dissolved nitrate may also be employed in conjunction with autoclaving, to obtain faster purification.

The invention is further illustrated by the following Examples:-

Example 1 (Comparative)

Natural flake graphite (10 grams; 99% carbon; 80% retained on a sieve of aperture 300μm diameter) was gently stirred for one hour with a mixture (90 grams; added at room temperature) of sulphuric acid, nitric acid and water, in weight proportions such that H_2SO_4; HNO_3; H_2O = 74:15:11.

The reaction mixture was poured onto a sintered glass filter plate to filter off the graphite derivative (probably $C_{24}^+.HSO_4^-.nH_2SO_4$) formed by reaction. This was washed for one hour with running water at room temperature (20°C) to free it from the molecular species H_2SO_4 and to introduce water molecules in place of H_2SO_4. The 'graphite bisulphate' thus formed is the starting material employed in Examples 2 to 4 later.

To exfoliate it, it was first drained from adherent water, then dried at 80°C for 3-4 hours, and finally conventionally flame-exfoliated at 1,000°C. The highly porous product (density 0.004 gram/cm^3) gave, on leaching with water under standard conditions, a leach solution of pH3.5 with a sulphate content equivalent to 440 parts per 10^6 of the exfoliated product.

Example 2

The graphite bisulphate of Example 1 (10 grams) was added to a 1M aqueous solution (90 grams) of nitric acid (i.e. HNO_3 content about 6% by weight), and the mixture was boiled for one hour. The solids were then removed, washed in running water, drained and dried at 80°C for 4 hours. On exfoliation the purified compound gave an expanded product which, in the leach test, gave a less acid solution (pH 4.5) than the exfoliated product of Example 1.

Example 3

The graphite compound of Example 1 (100 grams) was added with stirring to water (900 cm^3) contained in a one-litre autoclave, and the mixture was then heated with stirring at 30rpm at 120°C for one hour.

The solids were then removed from the autoclave, drained, and dried at 80°C for 4 hours. On exfoliation the purified compound gave an expanded product which, in the leach test of Example 1, gave a very weakly acid solution (pH6.4), of sulphate content equivalent to 50 parts per 10^6 of exfoliated material.

Example 4

The graphite compound of Example 1 (100 grams)

was added with stirring to a 1M-HNO_3 aqueous solution (900cm^3) contained in a one-litre autoclave, and the mixture was then heated with stirring at 30 rpm at 110°C for one hour.

The solids were then removed from the autoclave, drained, washed with running water at room temperature (20°C) for one hour and dried at 80°C for 3 hours. On exfoliation the purified compound gave an expanded product which, in the leach test of Example 1, gave a very weakly acid solution (pH 6.6) of sulphate content equivalent to 25 parts per 10^6 of exfoliated material.

CLAIMS

1. A method of purifying a graphite compound obtained by treating graphite with sulphuric acid under oxidising conditions and washing the product with water to replace with water the free sulphuric acid present in it, in which the water-washed product is further contacted with water, either at a temperature above 100°C under superatmospheric pressure or at a temperature above 30°C in the presence of dissolved nitric acid or a nitrate.

2. A method according to Claim 1, in which the water-washed product is heated in water at a temperature in the range 105-200°C under superatmospheric pressure.

3. A method according to Claim 1, in which the water-washed product is heated in water above 30°C in the presence of an amount of dissolved nitric acid or a nitrate such as to make the solution 0-1-2M in NO_3^-.

4. A method according to Claim 1, in which the water-washed product is heated at a temperature above 100°C and under superatmospheric pressure in the presence of dissolved nitric acid or a nitrate.

5. A method according to any preceding Claim, in which the weight ratio water-washed graphite compound: aqueous phase with which it is further contacted, is in the range 2:100 - 20:100.

6. A method of purifying a graphite compound obtained by treating graphite with sulphuric acid under oxidising conditions and washing the product with water to replace with water the free sulphuric acid present in it, substantially as described with reference to Example 2, 3 or 4 herein.

7. Exfoliated graphite obtained by exfoliation of a graphite compound purified by the method of any preceding Claim.

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ABSTRACT:

Expanded graphite compounds obtained by treating **graphite with sulphuric** acid under oxidising conditions, and **washing** the product with water to replace with water the free **sulphuric** acid present in it, contain bisulphate ions which are not removed on flash heat expansion (exfoliation) and are responsible for the slight corrosive capacity of material made by compacting the exfoliated stuff. Reduction of such corrosion can be achieved by subjecting the pre-exfoliated water- **washed graphite** compound to a further treatment with

water, in which there is employed water at a temperature above 100 DEG C under
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